# DIRECT POSITIVE PHOTOGRAPHIC MATERIALS AND A METHOD OF FORMING DIRECT POSITIVE IMAGES

## FIELD OF TECHNOLOGY

This invention concerns direct positive silver halide photographic materials and a method of forming direct positive images.

## PRIOR ART

Photographic processes for obtaining positive images directly without the need for a reversal process or negative film are well known.

The conventionally known methods used to form positive images with direct positive silver halide photographic materials can, if special cases are excluded, be divided into two main types, having regard to their practical use.

Thus, in methods of the first type a pre-fogged silver halide emulsion is used and a direct positive image is obtained after development by destroying the fogged nuclei (latent image) in the exposed part by means of solarization or a Herschel effect, for example.

In methods of the second type an unfogged internal latent image type silver halide emulsion is employed and a direct positive image is obtained after imagewise exposure by means of surface development either after or during a fogging process.

The above mentioned internal latent image type silver halide photographic emulsions are silver halide photographic emulsions of the type which have internal light-sensitive nuclei principally inside silver halide grains and they are such that the latent image is formed by the exposing light mainly within these grains.

The methods of the latter type generally have a higher sensitivity than methods of the former type and they are suitable for use in application where a high sensitivity is required. This invention concerns methods of the latter type.

Various techniques are already well known in this field. Thus the principal techniques are disclosed for example in U.S. Pat. Nos. 2,592,250, 2,466,957, 2,497,875, 2,588,982, 3,317,322, 3,761,266, 3,761,276 and 3,796,577 and in British Pat. Nos. 1,151,363, 1,150,553 and 1,011,062.

Comparatively high speed photographic materials of the direct positive type can be made using these known methods.

Furthermore, details of the mechanism by which the direct positive image is formed have been disclosed for example by T. H. James in *The Theory of the Photographic Process*, 4th Edition, Chapter 7, pp. 182 to 193, and in U.S. Pat. No. 3,761,276.

Thus, it is believed that fogging nuclei are formed selectively only on the surfaces of silver halide grains in the unexposed parts as a result of a surface desensitizing action originating from the so-called internal latent image which has been formed inside the silver halide grains by the initial imagewise exposure, and then the photographic image (direct positive image) is formed in the unexposed parts by means of what might be termed a normal surface development process.

Methods generally known as light fogging methods in which a second exposure is given to the whole of the light sensitive layer (for example, see British Pat. No. 1,151,363) and methods known as chemical fogging methods in which a nucleating agent is used are already known as methods used in the selective formation of the fogging nuclei. The latter method is disclosed for example on pages 76 to 78 of *Research Disclosure*, Vol. 151, No. 15162 (published in November 1976).

An internal latent image type silver halide photosensitive material can be subjected to a surface color development process after carrying out a fogging treatment or while carrying out a fogging treatment and then to bleaching and fixing processes (or a bleach-fix process) to form a direct positive color image. A water wash and/or stabilization treatment is normally carried out after the bleaching and fixing processes.

The development speed is slower and a longer processing time than that required for negative type materials is required to form direct positive images using light fogging or chemical fogging methods of this type and so conventionally the pH of the developer and/or the developer temperature has/have been raised to shorten the processing time. However, in general problems arise with rising minimum image density in the direct positive images obtained when the pH is raised. Furthermore, the developing agent itself is more liable to deteriorate due to aerial oxidation under conditions of high pH, and the pH is liable to fall as a result of the absorption of carbon dioxide gas from the atmosphere. This results in a considerable reduction in developer activity.

Other known means of raising the development speed in direct positive image formation include the use of hydroquinone derivatives (U.S. Pat. No. 3,227,552), and the use of mercapto compounds which have carboxylic acid groups or sulfonic acid groups (Japanese Patent Application (OPI) No. 170843/85 (the term "OPI" as used herein means a "published unexamined patent application")) but the use of these compounds has little effect and no way has yet been discovered for raising the maximum density of direct positive images effectively. The provision of a technique with which it is possible to obtain adequate maximum image density while processing with a low pH developer is therefore especially desirable.

On the other hand, there is a problem with direct positive photosensitive materials in that if the unexposed regions remaining when the image is exposed are narrow, the maximum image density is much lower in these regions than it is in wider unexposed regions. Consequently direct positive photosensitive materials tend to have lower resolving power than negative photosensitive materials and a means of overcoming this problem is also desirable.

Furthermore, a surface chemical sensitization treatment can be carried out in order to increase the maximum density of the resulting direct positive image, especially in the case of core/shell type silver halide emulsions, but surface chemical sensitization must normally be stopped at an appropriate level in order to avoid problems with rinsing minimum density which arises as a result of excessive chemical sensitization, with reduction in sensitivity and with the formation of false images in the parts which have been subjected to a high level of exposure. Moreover, the nuclei which are formed at this time by surface chemical sensitization are weak in comparison to those usually obtained with negative type materials and their stability with respect to the passage of time is very poor.

The addition of conventional well known stabilizers such as 4-hydroxy-6methyl--1,3,3a,7-tetrazaindene, 1-phenyl-5-mercaptotetrazole etc. has been investigated